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# Nucleosides and Nucleotides. Part 207: Studies in the Chemical Conversion of the 4-Carboxamide Group of 5-Amino-1-β-D-ribofuranosylimidazole-4-carboxamide (AICA-Riboside). Application for the Synthesis of 1-Deazaguanosine☆

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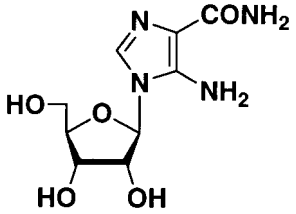
**Abstract**—A mild and versatile chemical conversion of the 4-carboxamide group of 5-amino-1-β-D-ribofuranosylimidazole-4-carboxamide (AICA-riboside) is described. The reaction of protected AICA-riboside with di-*tert*-butyl dicarbonate gave 5-[*N*,*N*-di-(*tert*-butoxycarbonyl)]-amino-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)imidazole-4-[*N*,*N*-di-(*tert*-butoxycarbonyl)]carboxamide in 71% yield. The resulting tetraBoc derivative was treated with sodium methoxide, benzylamine, or acetonitrile anion to give the corresponding methyl ester, *N*-benzylcarboxamide, or cyanoacetyl products. The 4-cyanoacetylimidazole derivative was converted into 1-deazaguanosine via an intramolecular cyclization. 

## Introduction

5-Amino-1-β-D-ribofuranosylimidazole-4-carboxamide (AICA-riboside; **1**) (Fig. 1) is a five-membered heterocyclic nucleoside, whose 5′-monophosphate is a central intermediate in the de novo biosynthesis of purine nucleotides.[1] For the development of biologically active nucleosides, **1** has been a valuable precursor for the chemical synthesis of nucleoside analogues, including 5-substituted imidazole nucleosides,[2–4] purine nucleosides,[5,6] 3-deazapurine nucleosides,[7,8] and imidazoazepine nucleosides.[9,10] However, the chemical conversions of **1** reported thus far mainly consist of modifications of its 5-amino group. Little is known about the chemical conversion of the 4-carboximide group of **1**, despite numerous synthetic efforts.

To date, only one useful chemical conversion of the 4-carboxamide group of **1** has been reported. Robins et al. converted **1** to *N*-succinimidyl 5-amino-1-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)imidazole-4-carboxylate through an alkaline hydrolysis of the 4-carboxamide group.[11] The *N*-hydroxysuccinimidyl ester derivative readily reacts with various amino acids to give amino acid–nucleoside conjugates.[11,12] Thus, the *N*-hydroxysuccinimidyl ester derivative, which is expected to react with various nucleophiles, is considered a useful precursor for the chemical conversion of the 4-carboximide group of **1**. However, harsh reaction conditions such as refluxing in 6N NaOH solution, normally incompatible for base-sensitive functional groups, are required for the alkaline hydrolysis of the 4-carboxamide group. In addition, the resulting sodium carboxylate derivative is known to be unstable because of the rapid evolution of carbon dioxide under lower pH conditions. In 1991, Bridson et al. reported the reaction of 1-(5-amino-1-β-D-ribofuranosylimidazole-4-carbonyl)-3,5-dimethylpyrazole, which is prepared from inosine, with amines or alcohols to give the amide or ester derivatives of 5-aminoimidazole nucleosides. However this method also used both strong basic and acidic conditions.[13]

In connection with our ongoing program on chemical modification of **1**, the development of a mild and versatile




**1 (AICA-riboside)**

**Figure 1.**

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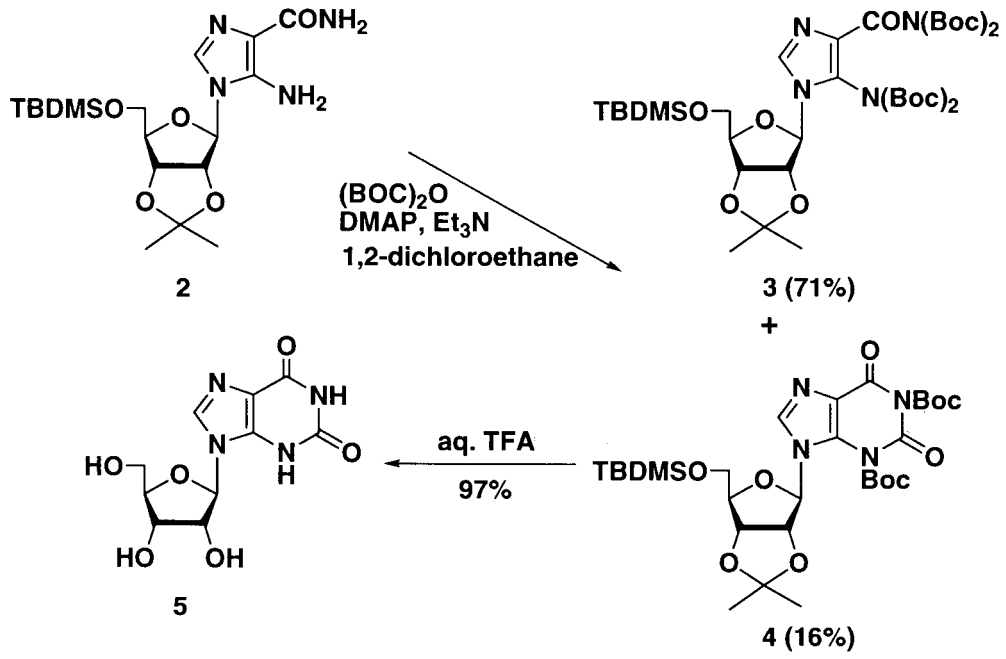
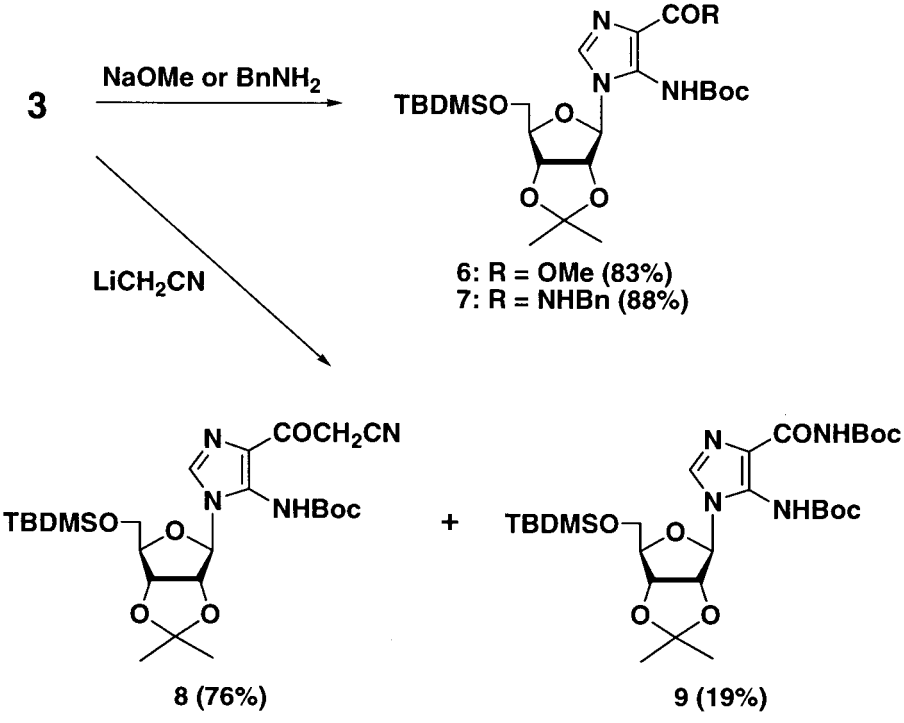
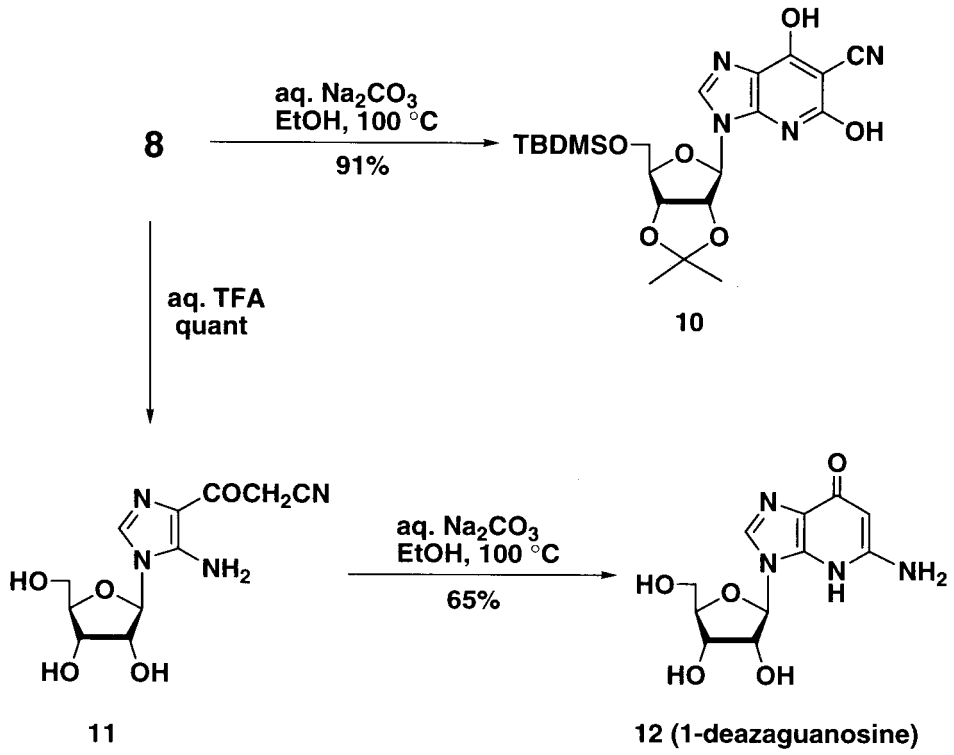



**Scheme 1.**

method for the chemical conversion of the 4-carboxamide group, which is expected to contribute giving valuable imidazole and purine nucleoside analogues, was needed. Thus far, several methods of facile conversion of primary amides into esters or substituted amides have been reported.[14–16] Among these pioneering methods, the one pot conversion of primary amides into *N*-acylimidodicarbonates by Davidsen et al.[15] seemed to be the most promising method for our purpose since it reacts with alcohols or amines to give the corresponding esters or amides. Reaction of **1** with di-*tert*-butyl dicarbonate to give *N*-acylimidodicarbonates would also act as a protection procedure for the reactive primary 5-amino group of the imidazole ring of **1**. We now describe the reaction of the protected AICA-riboside with di-*tert*-butyl dicarbonate, followed by nucleophilic substitution of an alcohol, amine, and carbanion. In addition, we demonstrate the facile synthesis of 1-deazaguanosine (**12**).




**Scheme 2.**




**Scheme 3.**

## Results and Discussion

Two different sets of reaction conditions were provided by Davidsen et al., for the preparation of *N*-acylimidodicarbonates.[15] One treats simple amides such as benzamide with di-*tert*-butyl dicarbonate in acetonitrile in the presence of a catalytic amount of dimethylaminopyridine (DMAP), the other treats amino acid derivative with di-*tert*-butyl dicarbonate in 1,2-dichloroethane in the presence of DMAP and triethylamine with heating. The first set of conditions was employed for the reaction with the AICA-riboside derivative **2**. The desired tetraBoc derivative **3** was obtained in 48% yield, along with 6% of protected xanthosine derivative **4**. In contrast, when the reaction was carried out under the latter conditions, the chemical yield of **3** was improved to 71% yield, although formation of **4** was also increased to 16% yield. No improvement was observed even when solvents and reaction temperatures, for example, were changed. The structure of **3** was confirmed by its FABMS, $^1$H, and $^{13}$C NMR spectra. A comparison of the $^1$H NMR spectrum of **3** with that of **2** revealed that the three broad singlets at 6.46 (one proton), 5.44 (two protons), and 5.13 ppm (one proton) due to the amide and amino protons of **2** had disappeared, and that three singlets at 1.47 (eighteen protons), 1.42 (nine protons), and 1.41 ppm (nine protons) due to *tert*-butyl groups had appeared in the $^1$H NMR spectrum of **3**. Since the $^1$H NMR spectrum of **4** was quite similar to that of **3** except for the number of proton signals due to the *tert*-butyl group, the structure of **4** was confirmed by deprotection of the protecting groups of **4** to give the free nucleoside. Thus, treatment of **4** with aqueous trifluoroacetic acid (TFA) gave xanthosine (**5**) in 97% yield, which has an $^1$H NMR spectrum identical with that of an authentic sample (Scheme 1).

The reaction of **3** with several nucleophiles was next examined (Scheme 2). When **3** was treated with sodium methoxide in methanol, the ester **6** was obtained in 83% yield. The *N*-benzylcarboxamide derivative **7** was also obtained in 88% yield by treatment of **3** with benzylamine in dichloromethane. These results provide strong evidence that **3** should be a versatile precursor to give the corresponding ester and amide derivatives from AICA-riboside. We then examined the reaction of **3** with carbon nucleophiles such as Grignard reagents and organolithiums. However, when **3** was treated with MeMgBr, EtMgBr, and MeLi, for example, no desired ketone product was obtained. Instead, the diBoc derivative **9** was the predominant product. Interestingly, the 4-cyanoacetyl derivative **8** was obtained in 76% yield, along with a 19% yield of the diBoc derivative **9**, by treatment of **3** with acetonitrile anion, prepared from acetonitrile and n-BuLi. The $^1$H NMR spectrum of **8** showed methylene proton signals at 4.15 and 4.06 ppm each as a doublet ($J$=19.6 Hz). Its FABMS spectrum, in which a molecular ion peak was detected at $m/z$ 537 as $MH^+$, and its IR spectrum, in which an absorption at 2260 $cm^{-1}$ due to a cyano group was observed, also indicated the structure of **8**. It is worth noting that **3** reacts with the carbanion to give the corresponding ketone, since Davidsen et al. reported that an *N*-acylimidodicarbonate derivative prepared from proline did not react with organometallic reagents such as Grignard reagents, organolithiums, and organocuprates in their original work.[15] In addition, the resulting **8** is thought to be a valuable precursor to give nucleoside derivatives such as 1-deazapurine nucleosides by further reactions.

In order to demonstrate this, conversion of **8** into 1-deazaguanosine (**12**), which has been previously prepared by

Townsend et al., via a glycosidation method,[17] was examined (Scheme 3). The target compound would be obtained by an intramolecular cyclization between the cyano group and the nitrogen atom at the 5 position. Initially, the intramolecular cyclization was attempted prior to deprotection of the Boc group. However, when **8** was treated under basic conditions, the 1-cyano-1-deaza-xanthosine derivative was obtained in 91% yield, but not the desired 1-deazaguanosine derivative. As can be seen from this result, the intramolecular cyclization between the carbanion at the 4 position and the carbonyl group of the Boc protecting group took place in preference to the requisite cyclization to give the 1-deazaguanosine derivative. Consequently, deprotection of the Boc group of **8** was conducted prior to the intramolecular cyclization. When **8** was treated with aqueous TFA, the Boc group was removed along with the isopropylidene and silyl protecting groups to give **11** in quantitative yield. To the best of our knowledge, this is the first example of protection and deprotection procedures for the 5-amino group of **1**. The 1-deazaguanosine (**12**) was obtained in 65% yield when **11** was heated under basic conditions. The analytical data of **12** were identical with those reported by Townsend et al.[17]

In conclusion, we have demonstrated that the protected AICA-riboside derivative **2** gives, upon treatment with di-*tert*-butyl dicarbonate, the tetraBoc derivative **3**, which reacts with sodium methoxide and benzylamine smoothly to give the corresponding ester and amide. In addition, **3** was converted into the 4-cyanoacetyl derivative **8** by treatment with acetonitrile anion. The resulting **8** was further converted into 1-deazaguanosine (**12**). This method allows for the mild and versatile chemical conversion of the 4-carboxamide group of **1**, which is expected to give not only 4-modified imidazole nucleosides, but also deazapurine nucleosides such as 1-deazaguanosine (**12**). Further investigations of the derivatization of **1** are underway.

## Experimental

### General methods

Physical data were measured as follows: Melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded at 270, 400, or 500 MHz and 100 or 125 MHz instruments in $CDCl_3$ or DMSO-$d_6$ as the solvent with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million ($\delta$), and signals are expressed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). All exchangeable protons were detected by addition of $D_2O$. TLC was done on Merck Kieselgel F254 precoated plates. Silica gel used for column chromatography was YMC gel 60A (70–230 mesh).

**5-[*N*,*N*-Di-(*tert*-butoxycarbonyl)]amino-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-imidazole-4-[*N*,*N*-di-(*tert*-butoxycarbonyl)]carboxamide (3) and $N^1$,$N^3$-di-(*tert*-butoxycarbonyl)-9-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-xanthine (4).** To a solution of **2**[8] (1.03 g, 2.5 mmol) in 1,2-dichloroethane (20 mL) containing DMAP (159 mg, 0.5 mmol) and triethylamine (1.4 mL, 10 mmol) was added di-*tert*-butyl dicarbonate (3.4 mL, 15 mmol) at room temperature. The reaction mixture was heated for 30 min at 75°C. The solvent was removed in vacuo, and the residue was purified by a silica gel column, eluted with hexane/AcOEt (9:1–1:2), to give **3** (1.44 g, 71% as a colorless oil) and **4** (0.25 g, 16% as a colorless oil).

**Physical data for 3.** FAB-LRMS *m/z* 813 ($MH^+$); FAB-HRMS calcd for $C_{38}H_{65}N_4O_{13}Si$ 813.4316, found 813.4296. $^1$H NMR ($CDCl_3$) 7.74 (s, 1H), 5.57 (d, 1H, *J*=2.7 Hz), 4.82 (dd, 1H, *J*=2.7, 6.2 Hz), 4.64 (dd, 1H, *J*=2.7, 6.2 Hz), 4.32 (q, 1H, *J*=2.7 Hz), 3.91 (dd, 1H, *J*=2.7, 11.5 Hz), 3.82 (dd, 1H, *J*=2.7, 11.5 Hz), 1.55 (s, 3H), 1.47 (s, 18H), 1.42 and 1.41 (each s, each 9H), 1.33 (s, 3H), 0.91 (s, 9H), 0.08 and 0.07 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) 162.40, 150.20, 149.10, 148.96, 132.03, 131.74, 129.00, 114.17, 90.85, 85.98, 85.87, 83.83, 83.76, 83.23, 80.52, 63.14, 27.66, 27.59, 27.35, 25.90, 25.33, 18.31, −5.42, −5.60.

**Physical data for 4.** FAB-LRMS *m/z* 439 ($MH^+$−Boc×2); FAB-HRMS calcd for $C_{19}H_{31}N_4O_6Si$ 439.2012, found 439.1992. $^1$H NMR ($CDCl_3$) 7.86 (s, 1H), 5.99 (d, 1H, *J*=3.3 Hz), 4.92 (dd, 1H, *J*=3.3, 6.0 Hz), 4.82 (dd, 1H, *J*=2.2, 6.0 Hz), 4.41 (dt, 1H, *J*=2.2, 3.3 Hz), 3.86 (dd, 1H, *J*=3.3, 11.3 Hz), 3.79 (dd, 1H, *J*=3.3, 11.3 Hz), 1.66 (s, 9H), 1.61 (s, 12H), 1.36 (s, 3H), 0.88 (s, 9H), 0.08 and 0.07 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) 155.17, 151.00, 148.15, 146.82, 136.18, 119.53, 113.91, 90.96, 86.72, 86.16, 86.12, 85.45, 81.22, 63.54, 28.00, 27.39, 27.26, 25.82, 25.23, 18.26, −5.46, −5.62.

**9-β-D-Ribofuranosylxanthine (5).** A solution of **4** (400 mg, 0.63 mmol) in 80% aqueous TFA (10 mL) was stirred for 2 h at 0°C. The solvent was removed in vacuo, and the residue was co-evaporated three times with ethanol. The residue was suspended to ethanol, and the resulting white precipitate was collected to give **5** (172 mg, 97% as a white solid). The spectral data for **5** was identical with the authentic sample.

**Methyl 5-[*N*-(*tert*-butoxycarbonyl)]amino-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)imidazole-4-carboxylate (6).** To a solution of **3** (510 mg, 0.63 mmol) in methanol (4 mL) was added 28% sodium methoxide solution (0.5 mL) at 0°C. The reaction mixture was stirred for 4.5 h at room temperature. The reaction mixture was partitioned between AcOEt and saturated aqueous $NH_4Cl$, and the organic layer was washed with $H_2O$, followed by brine. The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (3:1–1:3), to give **6** (274 mg, 83% as a colorless oil): FAB-LRMS *m/z* 528 ($MH^+$); FAB-HRMS calcd for $C_{24}H_{42}N_3O_8Si$ 528.2740, found 528.2745. $^1$H NMR ($CDCl_3$) 7.68 (s, 1H), 7.21 (br s, 1H, $D_2O$ exchangeable), 6.00 (d, 1H, *J*=2.0 Hz), 4.77 (m, 2H), 4.35 (m, 1H), 3.86 (s, 3H), 3.84 (dd, 1H, *J*=2.6, 11.2 Hz), 3.74 (dd, 1H, *J*=3.0, 11.2 Hz), 1.52 (s, 3H), 1.47 (s, 9H), 1.32 (s, 3H), 0.83 (s, 9H), 0.04 and 0.02 (each s, each 3H); $^{13}$C NMR ($CDCl_3$) 163.77, 152.75, 132.78, 132.28, 113.81, 92.27, 86.53, 86.05, 82.09, 80.82, 63.32, 51.52, 28.03, 27.27, 25.88, 25.47, 18.32, −5.48, −5.65.

**5-[*N*-(*tert*-Butoxycarbonyl)]amino-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-imidazole-4-(*N*-benzyl)carboxamide (7).** To a solution of **3** (406 mg, 0.5 mmol) in dichloromethane (4 mL) was added benzylamine (0.22 mL, 2.0 mmol), and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo, and the residue was purified by a silica gel column, eluted with hexane/AcOEt (5:1–1:1), to give **7** (265 mg, 88% as a white foam): FAB-LRMS *m/z* 603 ($MH^+$); FAB-HRMS calcd for $C_{30}H_{47}N_4O_7Si$ 603.3213, found 603.3229. $^1H$ NMR ($CDCl_3$) 7.76 (br s, 1H, $D_2O$ exchangeable), 7.57 (s, 1H), 7.31–7.23 (m, 6H), 6.11 (d, 1H, *J*=2.3 Hz), 4.76 (m, 2H), 4.55 (m, 2H), 4.38 (m, 1H), 3.83 (dd, 1H, *J*=3.0, 11.5 Hz), 3.73 (dd, 1H, *J*=3.3, 11.5 Hz), 1.52 (s, 3H), 1.48 (s, 9H), 1.33 (s, 3H), 0.82 (s, 9H), 0.05 and 0.02 (each s, each 3H); $^{13}C$ NMR ($CDCl_3$) 163.42, 153.18, 138.42, 131.43, 129.96, 128.55, 127.59, 127.24, 113.63, 92.75, 86.67, 86.08, 81.78, 80.97, 63.42, 42.60, 28.06, 27.25, 25.83, 25.54, 18.25, −5.53, −5.67.

**5-[*N*-(*tert*-Butoxycarbonyl)]amino-4-cyanoacetyl-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)imidazole (8) and 5-[*N*-(*tert*-butoxycarbonyl)]-amino-1-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)imidazole-4-[*N*-(*tert*-butoxycarbonyl)]carboxamide (9).** To a solution of acetonitrile (1.5 mL, 28.5 mmol) in THF (70 mL) was added n-BuLi (1.63 M in THF, 15.6 mL, 25.5 mmol) over 20 min at −78°C. To the resulting orange solution, a THF solution (30 mL) of **3** (4.14 g, 5.1 mmol) was added dropwise, and the whole was stirred for 1 h at the same temperature. The reaction was quenched by addition of saturated aqueous $NH_4Cl$, and the reaction mixture was partitioned between AcOEt and $H_2O$. The separated organic layer was washed with $H_2O$, followed by brine. The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo. The residue was purified by a silica gel column, eluted with hexane/AcOEt (5:1–1:1), to give **8** (2.1 g, 76% as a white foam) and 9 (533 mg, 19% as a white foam).

**Physical data for 8.** FAB-LRMS *m/z* 537 ($MH^+$); FAB-HRMS calcd for $C_{25}H_{41}N_4O_7Si$ 537.2744, found 537.2712. IR 2260 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 7.78 (br s, 1H, $D_2O$ exchangeable), 7.66 (s, 1H), 6.15 (d, 1H, *J*=1.8 Hz), 4.73 (m, 2H), 4.46 (m, 1H), 4.15 and 4.06 (each d, each 1H, *J*=19.6 Hz), 3.86 (dd, 1H, *J*=2.5, 11.5 Hz), 3.75 (dd, 1H, *J*=2.8, 11.5 Hz), 1.54 (s, 3H), 1.51 (s, 9H), 1.36 (s, 3H), 0.82 (s, 9H), 0.04 and 0.02 (each s, each 3H); $^{13}C$ NMR ($CDCl_3$) 183.94, 152.07, 132.99, 132.86, 127.35, 114.23, 113.72, 93.58, 87.07, 85.97, 82.70, 81.19, 63.53, 28.87, 27.98, 27.17, 25.76, 25.42, 18.20, −5.62, −5.76.

**Physical data for 9.** FAB-LRMS *m/z* 613 ($MH^+$); FAB-HRMS calcd for $C_{28}H_{49}N_4O_9Si$ 613.3268, found 613.3268. $^1H$ NMR ($CDCl_3$) 8.79 (br s, 1H, $D_2O$ exchangeable), 7.70 (br s, 1H, $D_2O$ exchangeable), 7.60 (s, 1H), 6.10 (d, 1H, *J*=2.3 Hz), 4.75 (m, 2H), 4.40 (m, 1H), 3.83 (dd, 1H, *J*=2.3, 11.2 Hz), 3.73 (dd, 1H, *J*=2.6, 11.2 Hz), 1.52 (s, 3H), 1.50 and 1.47 (each s, each 9H), 1.33 (s, 3H), 0.82 (s, 9H), 0.04 and 0.02 (each s, each 3H); $^{13}C$ NMR ($CDCl_3$) 161.19, 152.74, 149.38, 132.19, 131.69, 122.68, 113.70, 93.23, 86.84, 86.11, 82.20, 82.01, 81.13, 63.53, 28.03, 27.27, 25.84, 25.54, 18.28, −5.51, −5.68.

**6-Cyano-5,7-dihydroxy-3-(5-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)imidazo[4,5-*b*]pyridine (10).** A solution of **8** (300 mg, 0.56 mmol) in a mixture of EtOH (10 mL), 5% aqueous $Na_2CO_3$ (5 mL) was heated at 100°C for 2 h. The solvent was removed in vacuo, and the residue was dissolved in $H_2O$ (50 mL). The solution was neutralized with 1N HCl, and then activated charcoal was added to the aqueous solution until no UV absorption was observed in the supernatant. The solution including the activated charcoal was poured into a glass tube, and the activated charcoal was washed with $H_2O$. The desired **10** was then eluted with a mixture of 28% ammonium hydroxide/EtOH (3:7). The UV-absorbing fractions were combined, and the solvent was removed to give **10** (233 mg, 91%, crystallized from AcOEt): mp >300°C; FAB-LRMS *m/z* 462 ($M^+$); IR 2210 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$) 10.59 (br s, 1H, $D_2O$ exchangeable), 7.71 (s, 1H), 6.04 (d, 1H, *J*=2.9 Hz), 5.17 (m, 1H), 4.89 (m, 1H), 4.09 (m, 1H), 3.65 (dd, 1H, *J*=5.3, 11.2 Hz), 3.61 (dd, 1H, *J*=5.3, 11.2 Hz), 1.54 and 1.33 (each s, each 3H), 0.84 (s, 9H), 0.03 (s, 6H); $^{13}C$ NMR (DMSO-$d_6$) 173.03, 164.47, 134.06, 122.20, 120.94, 113.35, 87.72, 85.55, 83.16, 80.73, 79.49, 63.18, 26.86, 25.77, 25.31, 17.96, −5.47. Anal. Calcd for $C_{21}H_{30}N_4O_6Si{\cdot}1/4H_2O$: C, 54.00; H, 6.58; N, 11.99. Found: C, 53.82, H, 6.53; N, 12.14.

**5-Amino-4-cyanoacetyl-1-β-D-ribofuranosylimidazole (11).** A solution of **8** (2.73 g, 5.1 mmol) in 70% aqueous TFA (60 mL) was sitrred for 12 h at room temperature. The solvent was removed in vacuo, and the residue was co-evaporated three times with EtOH. The residue was purified by a silica gel column, eluted with EtOH in $CHCl_3$ (0–30%), to give **11** (1.4 g, 96%, crystallized from MeOH): mp 202–203°C; FAB-LRMS *m/z* 283 ($MH^+$); $^1H$ NMR (DMSO-$d_6$) 7.39 (s, 1H), 7.01 (br s, 2H, $D_2O$ exchangeable), 5.54 (d, 1H, *J*=6.7 Hz), 5.40 (d, 1H, *J*=6.4 Hz, $D_2O$ exchangeable), 5.36 (t, 1H, *J*=4.9 Hz, $D_2O$ exchangeable), 5.18 (d, 1H, *J*=4.3 Hz, $D_2O$ exchangeable), 4.27 (ddd, 1H, *J*=6.7, 6.4, 5.6 Hz), 4.13 (s, 2H), 4.04 (ddd, 1H, *J*=5.6, 4.3, 2.5 Hz), 3.93 (m, 1H), 3.59 (m, 2H); $^{13}C$ NMR (DMSO-$d_6$) 180.25, 146.84, 130.75, 118.32, 116.60, 87.50, 85.70, 72.76, 70.40, 61.10, 27.26. Anal. Calcd for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.85. Found: C, 46.71, H, 5.05; N, 19.68.

**5-Amino-3-(β-D-ribufuranosyl)imidazo[4,5-*b*]pyridin-7-one (1-deazaguanosine, 12).** In the same manner as described for **10**, **11** (240 mg, 0.85 mmol) was heated in a mixture of EtOH (10 mL), 5% aqueous $Na_2CO_3$ (5 mL) to give **12** (155 mg, 65%, crystallized from EtOH): mp 144–146°C (lit.[17] mp 148–150°C); $^1H$ NMR (DMSO-$d_6$) 7.94 (s, 1H), 5.80 (s, 1H), 5.76 (d, 1H, *J*=6.4 Hz), 5.56 (br s, 2H, $D_2O$ exchangeable), 5.49 (br s, 1H, $D_2O$ exchangeable), 5.29 (br s, 1H, $D_2O$ exchangeable), 5.05 (br s, 1H, $D_2O$ exchangeable), 5.52 (br t, 1H), 4.08 (br s, 1H), 3.89 (br s, 1H), 3.64 (dd, 1H, *J*=3.5, 12.1 Hz), 3.53 (dd, 1H, *J*=3.5, 12.1 Hz); $^{13}C$ NMR (DMSO-$d_6$) 157.99, 157.16, 147.11, 136.70, 119.06, 89.57, 87.15, 85.40, 72.99, 70.74, 61.80.

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